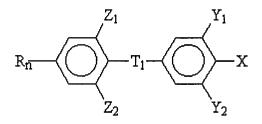
09/655,466 HRL033-B OA4

### APPENDIX A

#### <u>CLAIMS</u>

What is claimed is:

1. (Thrice Amended) Liquid crystal compounds having the general structure:



(Structure IV)

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wherein X is selected from the group consisting of OCF3 (trifluoromethoxy), and NCS (isothiocyanate);

 $T_1$  is a triple bond;

10  $Y_1$  and  $Y_2$  are a pair of substituents selected from the group consisting of H and F, and  $Y_1$ =  $Y_2$ ;

 $Z_1$  and  $Z_2$  are a pair of substituents selected from the group consisting of H and F, and  $Z_1$  =  $Z_2$ ; and,

at least one of the pairs  $Y_1$  and  $Y_2$  and  $Z_1$  and  $Z_2$  are substituted with F;

Rn is selected from the group consisting of an alkyl group having the general formula  $C_nH_{2n+1}$ , an alkenyl group having the general formula  $C_nH_{2n-1}$ , an alkoxy group having the general formula  $OC_nH_{2n+1}$ , an alkenoxy group having the general formula  $OC_nH_{2n-1}$ , and a group of the general structure

$$R_{\overline{X}}$$

# (Structure VII)

wherein  $R_x$  is selected from a group consisting of an alkyl group having the general formula  $C_xH_{2x+1}$ , an alkenyl group having the general formula  $C_xH_{2x-1}$ , an alkoxy group having the general formula  $OC_xH_{2x+1}$ , and an alkenoxy group having the general formula  $OC_xH_{2x-1}$ ; and,

wherein n is an integer greater than 0 and x is an integer greater than 0.

#### 2. (cancelled)

- 3. (original) A liquid crystal compound as set forth in claim 1, wherein  $R_n$  is selected from a group consisting of an alkyl group having the general formula  $C_nH_{2n+1}$ , an alkenyl group having the general formula  $C_nH_{2n-1}$ , an alkoxy group having the general formula  $OC_nH_{2n+1}$ , and an alkenoxy group having the general formula  $OC_nH_{2n-1}$  where n is approximately 2 to 12.
- 4. (original) A liquid crystal compound as set forth in claim 1, wherein  $R_x$  is selected from a group consisting of an alkyl group having the general formula  $C_xH_{2x+1}$ , an alkenyl

group having the general formula  $C_xH_{2x-1}$ , an alkoxy group having the general formula  $OC_xH_{2x+1}$ , and an alkenoxy group having the general formula  $OC_xH_{2x-1}$  where x is approximately 2 to 12.

- 5. (original) A liquid crystal compound as set forth in claim 1, wherein  $R_n$  is an alkenyl group having the general formula  $C_nH_{2n-1}$ .
- 6. (original) A liquid crystal compound as set forth in claim 1, wherein  $R_n$  is an alkenyl group having the general formula  $C_nH_{2n-1}$  where n ranges approximately from 2 to 12.
- 7. (once amended) Liquid crystal compounds having the general structure:

$$R_n$$
 $X_1$ 
 $X_2$ 
 $X_1$ 
 $X_2$ 
 $X_2$ 

# (Structure IV)

wherein X is selected from the group consisting of OCF3 (trifluoromethoxy), and NCS (isothiocyanate);

 $T_1$  is a triple bond;

 $Y_1$  and  $Y_2$  are a pair of substituents selected from the group consisting of H and F, and  $Y_1$ =  $Y_2$ ;  $Z_1$  and  $Z_2$  are a pair of substituents selected from the group consisting of H and F, and  $Z_1$  =  $Z_2$ ; and,

at least one of the pairs  $Y_1$  and  $Y_2$  and  $Z_1$  and  $Z_2$  are substituted with F;

Rn is selected from the group consisting of an alkyl group having the general formula  $C_nH_{2n+1}$ , an alkenyl group having the general formula  $C_nH_{2n-1}$ , an alkoxy group having the general formula  $OC_nH_{2n+1}$ , an alkenoxy group having the general formula  $OC_nH_{2n-1}$ , and a group of the general structure

$$R_{\overline{X}}$$

### (Structure VII)

wherein  $R_x$  is selected from a group consisting of an alkyl group having the general formula  $C_xH_{2x+1}$ , an alkenyl group having the general formula  $C_xH_{2x-1}$ , an alkoxy group having the general formula  $OC_xH_{2x+1}$ , and an alkenoxy group having the general formula  $OC_xH_{2x-1}$ ;

wherein n is an integer greater than 0 and x is an integer greater than 0; and A liquid crystal compound as set forth in claim 1, wherein  $R_n$  is an alkenyl group having the general formula  $C_xH_{2x-1}CH=CH-(CH_2)$ -.

8. (Twice Amended) Liquid crystal compounds having the general structure

$$R_{m} - \underbrace{ \begin{pmatrix} A_{1} & & Z_{1} & & Y_{1} \\ & & & & \\ A_{2} & & & Z_{2} & & Y_{2} \end{pmatrix}}_{X_{1}} - \underbrace{ \begin{pmatrix} Y_{1} & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ &$$

(Structure V)

wherein X is selected from the group consisting of F (fluoro), OCF<sub>3</sub>(trifluoromethoxy), and NCS (isothiocyanate);

T<sub>1</sub> is selected from the group consisting of a triple and a double covalent bond between two carbons;

T<sub>2</sub> is selected from the group consisting of a triple and a double covalent bond between two carbons; and,

 $T_1$  is not equal to  $T_2$  when  $T_1$  or  $T_2$  is a double bond;

 $Y_1$  and  $Y_2$  are a pair of substituents selected from the group consisting of H and F and  $Y_1$ =  $Y_2$ ;

 $Z_1$  and  $Z_2$  are a pair of substituents selected from the group consisting of H and F and  $Z_1$  =  $Z_2$ ;

 $A_1$  and  $A_2$  are a pair of substituents selected from the group consisting of H and F and  $A_1$ =  $A_2$ ;

at least one of the pairs  $Y_1$  and  $Y_2$ ,  $Z_1$  and  $Z_2$ , and  $A_1$  and  $A_2$  is substituted with F; and,  $R_m$  is selected from the group consisting of an alkyl group having the general formula  $C_mH_{2m+1}$ , an alkenyl group having the general formula  $C_mH_{2m-1}$ , an alkoxy group having

the general formula  $OC_mH_{2m+1}$ , and an alkenoxy group having the general formula  $OC_mH_{2m-1}$ , wherein m is an integer greater than 0; and,

wherein when  $T_1$  and  $T_2$  are both triple bonds and  $R_m$  is an alkyl group, one and only one of the pairs  $Y_1$  and  $Y_2$ ,  $Z_1$  and  $Z_2$ , and  $Z_1$  and  $Z_2$  and  $Z_3$  are both triple bonds and  $Z_3$  are both triple bonds and  $Z_4$  are both triple bonds and  $Z_4$  are alkyl group, one and only one of the pairs  $Z_1$  and  $Z_2$ , and  $Z_3$  are both triple bonds and  $Z_4$  are both triple bonds are both triple bonds and  $Z_4$  are both triple bonds are bon

9. (original) A liquid crystal compound as set forth in claim 8, wherein X is a substituted with F;

Y<sub>1</sub> and Y<sub>2</sub> are substituted with F; and,

 $Z_1$  and  $Z_2$  and  $A_1$  and  $A_2$  are H groups.

10. (original) A liquid crystal compound as set forth in claim  $\mathbf{8}$ , wherein  $T_1$  and  $T_2$  are triple bonds between two carbons.

11. (original) A liquid crystal compound as set forth in claim  $\mathbf{8}$ , wherein  $R_m$  is selected from a group consisting of an alkyl group having the general formula  $C_mH_{2m+1}$ , an alkenyl group having the general formula  $C_mH_{2m-1}$ , an alkoxy group having the general formula  $OC_mH_{2m+1}$ , and an alkenoxy group having the general formula  $OC_mH_{2m-1}$  where m is approximately 2 to 12.

12. (original) A liquid crystal compound as set forth in claim 8, wherein  $R_m$  is an alkenyl group having the general formula  $C_mH_{2m-1}$ .

13. (original) A liquid crystal compound as set forth in claim 8, wherein  $R_m$  is an alkenyl group having the general formula  $C_mH_{2m-1}$  where m ranges approximately from 2 to 12.

14. (original) A liquid crystal compound as set forth in claim 8, wherein  $R_m$  is an alkenyl group having the general formula  $C_mH_{2m-1}CH=CH-(CH_2)$ -.

15. (Thrice Amended) A eutectic mixture of liquid crystal compounds comprising at least two liquid crystal compounds, including at least one compound having the general structure

$$R_n$$
 $Z_1$ 
 $T_1$ 
 $X_2$ 
 $X_2$ 

(Structure IV)

wherein X is selected from the group consisting of OCF3(trifluoromethoxy), and NCS (isothiocyanate);

T<sub>1</sub> is a triple bond;

 $Y_1$  and  $Y_2$  are a pair of substituents selected from the group consisting of H and F and  $Y_1$ =  $Y_2$ ;

 $Z_1$  and  $Z_2$  are a pair of substituents selected from the group consisting of H and F and  $Z_1$  =  $Z_2$ ;

at least one of the pairs  $Y_1$  and  $Y_2$  and  $Z_1$  and  $Z_2$  are substituted with F;

 $R_n$  is selected from the group consisting of an alkyl group having the general formula  $C_nH_{2n+1}$ , an alkenyl group having the general formula  $C_nH_{2n-1}$ , an alkoxy group having the general formula  $OC_nH_{2n+1}$ , an alkenoxy group having the general formula  $OC_nH_{2n-1}$ , and a group of the general structure

$$R_{\overline{x}}$$

#### (Structure VII)

wherein  $R_x$  is selected from a group consisting of an alkyl group having the general formula  $C_xH_{2x+1}$ , an alkenyl group having the general formula  $C_xH_{2x-1}$ , an alkoxy group having the general formula  $-OC_xH_{2x+1}$ , and an alkenoxy group having the general formula  $-OC_xH_{2x-1}$ ; and,

wherein n is an integer greater than 0 and x is an integer greater than 0

16. (Twice Amended) A eutectic mixture of liquid crystal compounds comprising at least two liquid crystal compounds including at least one compound having the general structure

$$R_m$$
 $T_2$ 
 $T_1$ 
 $T_1$ 
 $T_2$ 
 $T_1$ 
 $T_2$ 
 $T_1$ 

(Structure V)

wherein X is selected from the group consisting of F (fluoro), OCF<sub>3</sub>(trifluoromethoxy), and NCS (isothiocyanate);

T<sub>1</sub> is selected from the group consisting of a triple and a double covalent bond between two carbons;

T<sub>2</sub> is selected from the group consisting of a triple and a double covalent bond between two carbons; and,

 $T_1$  is not equal to  $T_2$  when  $T_1$  or  $T_2$  is a double bond;

 $Y_1$  and  $Y_2$  are a pair of substituents selected from the group consisting of H and F and  $Y_1$ =  $Y_2$ ;

 $Z_1$  and  $Z_2$  are a pair of substituents selected from the group consisting of H and F and  $Z_1$  =  $Z_2$ ;

 $A_1$  and  $A_2$  are a pair of substituents selected from the group consisting of H and F and  $A_1$ =  $A_2$ ;

at least one of the pairs  $Y_1$  and  $Y_2$ ,  $Z_1$  and  $Z_2$ , and  $A_1$  and  $A_2$  is substituted with F; and,  $R_m$  is selected from the group consisting of selected from a group consisting of an alkyl group having the general formula  $C_mH_{2m+1}$ , an alkenyl group having the general formula  $C_mH_{2m-1}$ , an alkoxy group having the general formula  $OC_mH_{2m+1}$ , and an alkenoxy group having the general formula  $OC_mH_{2m-1}$ , wherein m is an integer greater than 0, and; wherein when  $T_1$  and  $T_2$  are both triple bonds and  $R_m$  is an alkyl group, one and only one of the pairs  $Y_1$  and  $Y_2$ ,  $Z_1$  and  $Z_2$ , and  $Z_3$ , and  $Z_4$  is substituted with  $Z_4$ .

17. (Twice Amended) A method for preparing liquid crystal compounds, comprising the steps of:

a) reacting an iodobenzene as shown in Structure 1 with trimethylsilyl acetylene in the presence of a catalyst and an amine to produce an trimethylsilylacetyl derivative as shown in structure 2;

$$R_n \longrightarrow Z_1$$
 $Z_1$ 
 $Z_2$ 

(Structure 1)

$$R_n$$
  $\longrightarrow$   $S_i$   $\longrightarrow$   $S_i$   $\longrightarrow$   $S_i$ 

(Structure 2)

b) isolating the trimethylsilylacetyl derivative shown in structure 2 from the reaction of the iodobenzene shown in structure 1 and trimethylsilylacetylene in the presence of the catalyst and the amine;

c) reacting the trimethylsilylacetyl derivative shown in structure 2 with a base to remove trimethyl silane and to give an unsubstituted product as shown in structure 3;

$$\mathbb{R}_{n}$$
  $\longrightarrow$   $\mathbb{Z}_{2}$   $\mathbb{Z}_{2}$ 

(Structure 3)

- d) isolating the unsubstituted product as shown in structure 3 from the reaction of the trimethylsilylacetyl derivative shown in structure 2 with the base;
- e) reacting the unsubstituted product as shown in structure 3 with a brominated, substituted benzene as shown in structure 3a to give a tolane product as shown in structure 4;

$$P_1$$
 $P_1$ 
 $P_2$ 
 $P_1$ 

(Structure 3a)

$$R_n$$
 $X_1$ 
 $X_2$ 
 $X_2$ 
 $X_2$ 

(Structure 4)

f) isolating the tolane product shown in structure 4 from the reaction of the unsubstituted product as shown in structure 3 with the brominated, substituted benzene brominated, substituted benzene shown in structure 3a;

wherein X is selected from the group consisting of F (fluoro), CN (cyano),

OCF<sub>3</sub>(trifluoromethoxy), and NCS (isothiocyanate);

 $T_1$  is a triple bond;

 $Y_1$  and  $Y_2$  are a pair of substituents selected from the group consisting of H and F, and  $Y_1 = Y_2$ ;

 $Z_1$  and  $Z_2$  are a pair of substituents selected from the group consisting of H and F, and  $Z_1$  =  $Z_2$ ; and,

At least one of the pairs  $Y_1$  and  $Y_2$  and  $Z_1$  and  $Z_2$  is substituted with F;

 $R_n$  is selected from the group consisting of an alkyl group having the general formula  $C_nH_{2n+1}$ , an alkenyl group having the general formula  $C_nH_{2n-1}$ , an alkoxy group having the general formula  $OC_nH_{2n+1}$ , an alkenoxy group having the general formula  $OC_nH_{2n-1}$ , a group of the general structure

$$R_2$$

and a group of the general structure

$$R_2$$
— $\bigcirc$ O

wherein  $R_x$  for both structures is selected from a group consisting of an alkyl group having the general formula  $C_xH_{2x+1}$ , an alkenyl group having the general formula  $C_xH_{2x-1}$ , an alkoxy group having the general formula  $OC_xH_{2x+1}$ , and an alkenoxy group having the general formula  $OC_xH_{2x-1}$  and wherein n is an integer and x is an integer.

18. (original) The method for preparing liquid crystal compounds as set forth in claim 17, wherein the catalyst in steps a) and e) is Pd(Ph<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI.

19. (original) The method for preparing liquid crystal compounds as set forth in claim 17, wherein the amine in steps a) and e) is triethylamine.

20. (original) The method for preparing liquid crystal compounds as set forth in claim 17, wherein the base in step c) is NaOH.

- 21. (Twice Amended) A method for preparing liquid crystal compounds, comprising the steps of:
  - a) reacting an iodobenzene as shown in Structure 5 with trimethylsilyl acetylene in the presence of a catalyst and an amine to produce an trimethylsilylacetyl derivative as shown in structure 6;

$$R_m - A_1$$

$$A_2$$

(Structure 5)

$$R_m$$
  $A_1$   $A_2$   $A_2$ 

(Structure 6)

- b) isolating the trimethylsilylacetyl derivative shown in structure 6 from the reaction of the iodobenzene shown in structure 5 and trimethylsilylacetylene in the present of the catalyst and the amine;
- c) reacting the trimethylsilylacetyl derivative shown in structure 6 with a base to
  remove trimethyl silane and to give an unsubstituted product as shown in structure
  7;

$$R_m$$
 $A_1$ 
 $A_2$ 

(Structure 7)

- d) isolating the unsubstituted product as shown in structure 7 from the reaction of the trimethylsilylacetyl derivative shown in structure 6 with the base;
- e) reacting the unsubstuted product as shown in structure 7 with a substituted bromoiodobenzene as shown in structure 7a in the presence of a catalyst, an amine, and triphenylphosphine to prepare a brominated, substituted tolane product shown in structure 8;

$$I - \underbrace{ \begin{array}{c} Z_1 \\ \\ Z_2 \end{array}} Br$$

### (Structure 7a)

$$R_m$$
  $A_1$   $Z_1$   $B_r$   $Z_2$ 

### (Structure 8)

- f) isolating the brominated, substituted tolane product shown in structure 8 from the reaction of the unsubstuted product as shown in structure 7 with the substituted bromoiodobenzene as shown in structure 7a in the presence of the catalyst, the amine, and triphenylphosphine;
- g) reacting the brominated, substituted tolane product shown in structure 8 with trimethylsilylacetylene in the presence of the catalyst, the amine, and

triphenylphosphine to produce a trimethylacetyl derivative as shown in structure 9;

$$R_m$$
 $A_1$ 
 $Z_1$ 
 $Z_1$ 
 $Z_2$ 

# (Structure 9)

- h) isolating the trimethylacetyl derivative shown in structure 9 from the reaction of the brominated, substituted tolane product shown in structure 8 with trimethylsilylacetylene in the presence of the catalyst, the amine, and triphenylphosphine;
- i) reacting the trimethylsilylacetyl derivative shown in structure 9 with a base to remove trimethylsilane and produce an unsubstituted product as shown in structure 10;

$$R_m$$
 $A_1$ 
 $A_2$ 
 $A_2$ 
 $A_2$ 
 $A_2$ 
 $A_2$ 
 $A_3$ 
 $A_4$ 
 $A_4$ 
 $A_5$ 
 $A_5$ 

# (Structure 10)

j) isolating the unsubstituted product shown in structure 10 from the reaction of the trimethylsilyl derivative shown in structure 9 with the base; k) reacting the unsubstituted product shown in structure 10 with a substituted bromobenzene as shown in structure 10a in the presence of a catalyst, an amine, and triphenylphosphine to produce a bis-tolane product as shown in structure 11;

$$\operatorname{Br} - \bigvee_{Y_2}^{Y_1} X$$

(Structure 10a)

$$R_{m} - \bigvee_{A_{2}}^{A_{l}} - \bigvee_{Z_{2}}^{Z_{l}} - X$$

(Structure 11)

l) isolating the bis-tolane product shown in structure 11 from the reaction of the unsubstituted product shown in structure 10 with the substituted bromobenzene shown in structure 10a in the presence of the catalyst, the amine, and triphenylphosphine;

wherein for the structures shown, X is selected from the group consisting of F (fluoro), CN (cyano), OCF<sub>3</sub>(trifluoromethoxy), and NCS (isothiocyanate);

 $T_1$  is selected from the group consisting of a triple and a double covalent bond between two carbons;

T<sub>2</sub> is selected from the group consisting of a triple and a double covalent bond between two carbons; and,

 $T_1$  is not equal to  $T_2$  when  $T_1$  or  $T_2$  is a double bond;

 $Y_1$  and  $Y_2$  are a pair of substituents selected from the group consisting of H and F and  $Y_1$ =  $Y_2$ ;

 $Z_1$  and  $Z_2$  are a pair of substituents selected from the group consisting of H and F and  $Z_1$  =  $Z_2$ ;

 $A_1$  and  $A_2$  are a pair of substituents selected from the group consisting of H and F and  $A_1$ =  $A_2$ ;

at least one of the pairs  $Y_1$  and  $Y_2$ ,  $Z_1$  and  $Z_2$ , and  $A_1$  and  $A_2$  is substituted with F; and,  $R_m$  is selected from the group consisting of selected from a group consisting of an alkyl group having the general formula  $C_mH_{2m+1}$ , an alkenyl group having the general formula  $C_mH_{2m-1}$ , an alkoxy group having the general formula  $OC_mH_{2m+1}$ , and an alkenoxy group having the general formula  $OC_mH_{2m-1}$  and wherein m is an integer.

- 22. (original) The method for preparing liquid crystal compounds as set forth in claim 21, wherein the catalyst in steps a), e), g), and k) is Pd(Ph<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI.
- 23. (original) The method for preparing liquid crystal compounds as set forth in claim 21, wherein the amine in steps a), e), g), and k) is triethylamine.

24. (original) The method for preparing liquid crystal compounds as set forth in claim 21, wherein the base in steps c) and i) is NaOH.